

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF DIMETHYL TEREPHTHALATE

(71) We, TEIJIN HERCULES CHEMICAL CO. LTD., a Japanese body corporate, of 1—1, 2-chome, Uchisaiwai-cho, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the direct preparation of dimethyl terephthalate.

Alkyl esters of aromatic carboxylic acids, particularly dimethyl terephthalate (DMT), are valuable compounds used as the starting materials for fibre-and film-forming polyesters, and are produced in large quantities on an industrial scale.

In the conventionally employed industrial methods for making the alkyl esters of aromatic carboxylic acids, oxidisable aromatic compounds containing aliphatic substituents such as methyl groups (for example *p*-xylene) or their partial oxidation derivatives are first oxidised with nitric acid or a gas containing molecular oxygen to be converted to aromatic carboxylic acids, and then the acids are esterified with lower aliphatic alcohols such as methanol. It is clear that if the alkyl esters could be formed directly from the oxidisable aromatic compounds and the aliphatic alcohols there would be a considerable industrial advantage.

Various proposals have already been made for obtaining the alkyl esters of aromatic carboxylic acids directly from the corresponding oxidisable aromatic compounds, but none has proved to be industrially advantageous.

For example, U.S. Patent Specification No. 3,047,612 discloses a process for the direct preparation of methyl esters of aromatic polycarboxylic acids, which process comprises contacting polyalkyl-substituted aromatic hydrocarbons with a gas containing molecular oxygen in the presence of a relatively large amount

of methanol, assisted by the catalytic action of a polyvalent heavy metal. However, when the substituent group on the aromatic compound is other than a group which is as easily oxidisable as an isopropyl group, e.g. a methyl group, a bromine compound must be used as the catalyst promoter. This causes severe corrosion of the apparatus, which can be prevented only by using expensive materials such as titanium for the apparatus. Furthermore, by-products are formed in large quantities due to the presence of the bromine compound, and the desired product, i.e. the methyl ester of the aromatic polycarboxylic acid, is highly coloured. The methanol which is used in relatively large quantities, also is consumed in considerable amounts by undesirable side reactions, and the efficiency of the reaction is drastically reduced.

Another U.S. Patent, No. 2,879,289, has proposed the oxidation of an alkylbenzene with a gas containing molecular oxygen in the presence of a lower aliphatic alcohol, as a method for making an alkyl ester of a benzenecarboxylic acid by a single-stage reaction. This prior art method is better than the first-mentioned, particularly in that it dispenses with the bromine compound.

U.S. Patent No. 2,879,289 teaches that a catalyst is not essential to the method, but, if desired, compounds of cobalt, manganese, cerium, vanadium, lead, chromium and iron may be used for that purpose. Furthermore, the specification states that a cobalt compound alone is used in most cases as the preferred catalyst and most of the working Examples illustrate the use of such a catalyst.

According to our studies, however, when a cobalt compound alone is used as a catalyst, various by-products, including high-boiling point, tar-like substances, are formed in substantial quantities, and consequently the selective conversion of a methyl-substituted aromatic compound to the corresponding aromatic

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carboxylic acid ester is low. Also when methanol is used as the lower aliphatic alcohol, the methanol is oxidised and decomposed to produce large quantities of carbon dioxide, carbon monoxide, formaldehyde, formic acid and methyl formate, causing heavy loss of the methanol.

The present invention provides a process for the direct conversion of oxidisable aromatic compounds to dimethyl terephthalate with high selectivity and fast reaction rates without using a catalyst promoter such as a bromine compound and yet while reducing the oxidation and decomposition of methanol.

According to the invention there is provided a process for the direct preparation of dimethyl terephthalate which comprises contacting molecular oxygen with a liquid phase reaction mixture comprising a catalyst, methanol and at least one aromatic compound selected from *p*-xylene and partial oxidation derivatives thereof, thus oxidising the methyl groups and/or partial oxidation derivatives thereof of the aromatic compound to carboxylic acid groups which are esterified *in situ* by the methanol to produce dimethyl terephthalate wherein the reaction is performed:

(1) in the substantial absence of halogen and halogen-containing compounds;

(2) while maintaining the concentration of methanol in the reaction mixture at 0.5 to 15% by weight;

(3) in the presence of a catalyst composed of (A) manganese metal or a manganese compound soluble in the reaction mixture and (B) at least one metal or metal compound selected from cobalt, nickel, cobalt compounds which are soluble in the reaction mixture and nickel compounds which are soluble in the reaction mixture, the weight ratio of (A) to (B), each calculated as the metal, being from 97:3 to 1:99 and the total concentration of (A) and (B), calculated as the metals, in the liquid phase reaction mixture being 100 to 10000 ppm when (B) is cobalt or a cobalt compound and 100 to 5000 ppm when (B) is nickel or a nickel compound;

(4) at a temperature of 160 to 280°C.

When operating in accordance with the invention, formation of by-products such as high temperature-boiling point substances is drastically reduced, loss of the methanol is reduced and dimethyl terephthalate is obtained with high selectivity and in high yield.

A characteristic feature of the process of the invention is the use of specified concentrations of a catalyst composed of the two components (A) and (B) in certain ratios of (A):(B). As later demonstrated by Examples and Controls, compared with the cases using other catalysts or catalyst concentrations, the invention makes possible an increase in:

(i) yield of the effective product based on the starting aromatic compound,

(ii) yield of the effective product based on the methanol, and

(iii) production rate of the dimethyl terephthalate.

The aromatic compound to be used as starting material in the process of the invention is *p*-xylene and/or a partial oxidation derivative thereof. Oxidation derivatives of *p*-xylene which may be used include *p*-toluic acid, *p*-tolualdehyde, methyl *p*-toluate and methyl *p*-formylbenzoate. Mixtures of *p*-xylene and partial oxidation derivatives thereof may be used as the starting material in the process.

The Components (A) and (B) should be soluble in the liquid-phase reaction mixture or should be convertible to a form in which they are soluble in the reaction mixture.

Preferred examples of the catalyst components (A) and (B) are as follows:

(1) manganese salts, cobalt salts, or nickel salts of aliphatic carboxylic acids such as formic, acetic, propionic, butyric, stearic, palmitic, oleic and linoleic acids;

(2) manganese salts, cobalt salts, or nickel salts of aromatic carboxylic acids such as benzoic and toluic acids;

(3) manganese salts, cobalt salts, or nickel salts of alicyclic carboxylic acids such as naphthenic acid;

(4) complex salts of manganese, cobalt, or nickel such as acetylacetonate, methyl acetoacetate, and ethyl acetoacetate;

(5) manganese metal, cobalt metal, or nickel metal, and

(6) various inorganic compounds of manganese, cobalt or nickel, such as carbonates, oxides and hydroxides.

Of the above-named, acetates, benzoates, toluates and naphthenates of manganese, cobalt, and nickel can be used with particularly favourable results. Such salts generally are easily available and readily soluble in the reaction mixture.

When the component (B) is cobalt metal or a cobalt compound, the weight ratio of (A):(B) preferably is 95:5 to 2:98, but when the component (B) is nickel metal or a nickel compound the weight ratio of (A):(B) preferably is 95:5 to 5:95.

When component (B) is cobalt metal or a cobalt compound the total concentration of (A) and (B) in the liquid-phase reaction mixture preferably is 200 to 8,000 ppm, but when the component (B) is nickel or a nickel compound the total concentration of (A) and (B) preferably is 200 to 4,000 ppm in each case calculating the components (A) and (B) as the metal.

(In this specification "ppm" denotes the total parts by weight of the components (A) and (B) calculated as the corresponding

metals, per million parts by weight of the reaction mixture, while the term "effective products" is used herein to denote not only dimethyl terephthalate but also oxidation intermediates which can be converted finally to dimethyl terephthalate by oxidation and/or esterification).

When the component (B) is cobalt metal or a cobalt compound the reaction temperature preferably is from 160° to 240°C, especially 170 to 230°C, but when the component (B) is nickel metal or a nickel compound the reaction temperature preferably is from 170 to 270°C especially 180 to 250°C.

When practicing the present invention under such conditions the yield of effective products based on both the starting aromatic compound and methanol used, as well as the rate of formation of the effective products can be significantly improved.

Furthermore, it is advantageous according to the invention to maintain the concentration of the methanol in the liquid-phase reaction mixture within the range of 0.5 to 10%, especially 0.5 to 8% by weight, during the reaction. When the concentration of methanol is below 0.5% by weight the yield of dimethyl terephthalate is undesirably reduced. On the other hand, if the concentration of methanol exceeds 15% by weight oxidation and decomposition of the methanol takes place vigorously not only to increase the loss of methanol but also to interfere with the smooth progress of the desired reactions.

The temperature and pressure conditions for the reaction should desirably prevent rapid evaporation of the methanol and preferred pressure conditions normally are from 1 to 200 kg/cm²G, although the pressure can vary depending on the reaction temperature.

In order to maintain the concentration of methanol in the liquid-phase reaction mixture at 0.5 to 15% by weight, methanol is continuously supplied to the reaction system either

in liquid or gaseous state, preferably in liquid state, while the reaction is in progress, with industrial advantage.

The gas containing molecular oxygen used as oxidising agent according to the invention, can be pure oxygen, air, air with increased oxygen concentration, air diluted with exhaust gas from the reaction, air diluted with an inert gas such as carbon dioxide or nitrogen or a gaseous mixture of an inert gas such as carbon dioxide or nitrogen with oxygen. Of these, air is the cheapest and is preferred. The gas can be contacted with the liquid phase reaction mixture by such means as blowing it into the reaction mixture.

The process of the invention need use no aliphatic monocarboxylic acid solvent such as acetic acid which has been conventionally used in the oxidation of alkyl-substituted aromatic compounds, simply because such solvent is unnecessary.

The process of the invention may be practiced either batchwise or continuously.

The reaction product resulting from the process contains, other than the dimethyl terephthalate, unreacted starting material, intermediate products, and by-products. Consequently it is desirable to separate the components of the reaction product by means known *per se*, such as distillation, and to recycle the unreacted starting material and intermediate products to the reaction system.

The dimethyl terephthalate separated from the reaction product may be further refined if desired, by such means as recrystallisation and distillation.

The invention will be explained in more detail by reference to the Examples and Controls which follow.

In the Examples, "yield of effective products based on PX" and "yield of effective products based on methanol" were calculated according to the formulae [I] and [II] below, respectively.

Yield of effective products based on PX =

$$\frac{\text{DMT and the intermediates convertible to DMT by further oxidation and/or esterification (mmol)}}{\text{Consumed PX (mmol)}} \times 100 \text{ [I]}$$

Yield of effective products based on methanol =

$$\frac{\text{number of carbomethoxy groups contained in DMT and the intermediates convertible to DMT upon further oxidation and/or esterification (mg equivalent)}}{\text{Consumed methanol (mmol)}} \times 100 \text{ [II]}$$

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Example A.

A 500-ml titanium autoclave equipped with an exhaust gas condenser, stirrer, gas inlet, and

a methanol inlet was charged with 200 g of *p* - xylene (PX), 5 g of *p* - toluic acid (PTA), and cobalt acetate and manganese

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acetate containing Co and Mn of the amounts specified for each run in Table 1 (the total concentration of the catalyst being 493 ppm in all runs). Air was blown into the autoclave at such a rate as would make the flow rate at the exit 5.5 liters/min., at 230°C. under a pressure of 30 kg/cm²G and high-speed stirring. After the oxygen absorption started, methanol was fed into the reaction system at a rate of 5 g/min. During the reaction time (4 hours) the conditions were maintained constant. The condensable gas which failed to be condensed in the exhaust gas condenser was passed through an exhaust gas-absorbing bottle, and trapped as dissolved in N,N-dimethyl formamide. The methanol concentration in the reaction mixture was maintained at approximately 4.4 wt %.

After the reaction was completed, the reaction mixture was cooled and withdrawn. The weight and composition of the reaction mixture and condensed liquid, and also the composition of the exhaust gas-absorbing liquid, were measured. From the measured values, the yield of the effective products (in-

clusive of the intermediate products which are convertible to DMT through further oxidation and esterification) based on the starting PX, as well as that based on the methanol, were determined, using the already given equations (I) and (II), respectively.

More specifically, the compounds measured, as included within the "effective product" based on the PX, were as follows: *p*-tolualdehyde, *p*-toluic acid and the methyl ester thereof, 4 - carboxybenzaldehyde and its methyl ester, terephthalic acid its mono- and dimethyl esters, and R-f-phenylene-COOH, f-phenyl-R', R and R' being any of CH₃, COOH, and COOCH₃.

Of the above-named compounds, those containing carbomethoxy group or groups constitute the "effective product" for the calculation of the yield based on the methanol.

The DMT formed (mmol) in the reaction mixture in each run was divided by the reaction time (hrs) to denote the formation rate of DMT. The results of those calculations are shown also in Table 1 below.

TABLE 1

Run No.	Catalyst		Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr)
	Mn(mgr)	Co (mgr)			
A-1 (Control)	0	100	66.8	39.5	44.4
A-2 (Example)	5	95	82.8	62.3	55.2

Example B.

PX, cobalt naphthenate, and manganese naphthenate were fed into a tank and mixed by stirring to serve as the initial mixture to be oxidized and esterified.

70 Parts by weight of the mixture was fed into a bubbling tower provided with a feed inlet at the middle part, a product outlet at the bottom, gas and methanol inlets near the bottom, and a gas outlet at the top. Air was blown into the tower through the gas inlet at a rate of 550 liters/min., at the temperature of 180°C. and pressure of 25 kg/cm²G. to initiate the oxidation. After the reaction started, PX and methanol were fed into the system at the rates of, respectively, 0.22 wt. parts/min. and 0.23 wt. parts/min. Simultaneously, withdrawal of the product from the

bottom of the tower was started at such a rate as would maintain the liquid level in the tower constant. The exhaust gas was led to a condenser from the gas outlet, and whereat the condensable gases of methanol, water, PX, and the like were condensed and recovered, the remnant being discharged into the atmosphere.

The operation under the described conditions were stably continued for 24 hours. In the meantime, the methanol concentration in the reaction mixture was maintained at approximately 7.7 wt %. Precisely determining the components and analysing the samples, the formation rate of DMT and the yields in each run were calculated, with the results as given in Table 2 below.

TABLE 2

Run No.	Catalyst's Concentration in Reaction Mixture		Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (wt part/hr.)
	Mn (ppm)	Co (ppm)			
B-1 (Control)	0	140	73.3	43.4	7.7
B-2 (Example)	6	134	85.4	67.7	9.8
B-3 (Control)	140	0	79.6	40.6	6.5

Example C.

The same autoclave as employed in Example A was used for the experiments with the operation procedures similar to Example A, except that the initial feed was composed of 200 g of PX, 5 g of PTA, and manganese acetate and cobalt acetate of the amount as would make the total concentration of Mn and Co as the metals 550 ppm. The ratio between the

two catalytic components was as specified in Table 3. The reaction temperature was 200°C., the pressure was 15 kg/cm²G, flow rate of air at the exit was 2.0 liters/min., feed rate of mixed liquid of methanol and PX (mixing ratio=4:1 by volume) was 100 ml/hr., and the reaction time was 4 hours.

The results of the reaction were as shown also in Table 3.

TABLE 3

Run No.	Mn:Co (weight ratio)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
C-1 (Control)	0:100	72.9	43.7	30.1
C-2 (do)	0.2:99.8	75.2	48.6	35.3
C-3 (do.)	0.6:99.4	76.2	55.7	39.7
C-4 (Example)	5:95	85.0	64.4	45.5
C-5 (do.)	10:90	85.6	65.3	44.2
C-6 (do.)	25:75	84.7	64.3	43.0
C-7 (do.)	50:50	79.3	58.3	42.4
C-8 (do.)	75:25	77.6	51.2	42.0
C-9 (do.)	97:3	76.1	43.8	41.3
C-10 (Control)	98.5:1.5	75.4	40.5	40.9
C-11 (do.)	100:0	75.0	39.8	40.5

Example D.

The same autoclave as that used in Example A was similarly operated for the experiments. The initial feed was composed of 200 g of PX, 5 g of PTA, and manganese acetate and cobalt acetate of the amounts as would make the sum concentration of Mn and Co calculated as the metals the value specified for each run in Table 4. The weight ratio of Mn to

Co was invariably 5:95. The reaction temperature was 200°C., the pressure was 15 kg/cm²G, flow rate of air at the exit was 2.0 liters/min., feed rate of the mixed liquid of methanol and PX (mixing ratio=4:1 by volume) was 100 ml/hr., and the reaction time was 4 hours.

The results were as shown in Table 4.

TABLE 4

Run No.	Mn + Co Catalyst Concentration (ppm)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
D-1 (Example)	100	76.2	46.3	28.4
D-2 (do.)	288	80.1	52.2	39.8
D-3 (do.)	550	84.8	64.3	44.7
D-4 (do.)	1000	85.1	64.4	47.2
D-5 (do.)	8000	80.0	52.2	30.6
D-6 (Control)	12000	74.8	40.7	24.6
D-7 (do.)	50000	60.3	26.6	1.1

Example E.

The same autoclave as used in Example A was used in the experiments operated in the manner similar to Example A. The initial feed was composed of 200 g of PX, 5 g of PTA, 50 mg of manganese acetate, and 447 mg of cobalt acetate (the total concentration of the catalyst calculated as the metals was 493

ppm). The other conditions, i.e., reaction temperature, pressure, feed rate of the methanol-PX mixed liquid (mixing ratio=4:1 by volume), and the flow rate of air at the exit, were varied for each run as shown in Table 5. The results of the experiments are also given in Table 5 below.

TABLE 5

Run No.	Temp. (°C.)	Pres. (kg/cm ² G)	Methanol + PX Feed Rate (ml/hr.)	Flow Rate of Air at Exit (l/min.)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
E-1 (Control)	120	3.0	50	1.5	The reaction failed to progress satisfactorily		
E-2 (do.)	140	3.5	50	1.5	86.1	36.4	0.5
E-3 (Example)	160	6.0	50	1.5	85.9	46.2	5.2
E-4 (do.)	180	10	50	1.5	85.6	62.3	23.0
E-5 (do.)	200	15	100	2.0	85.4	65.1	45.1
E-6 (do.)	240	20	100	2.0	75.8	65.0	56.2
E-7 (Control)	285	35	100	2.0	52.3	62.1	59.5

Example F.

The same autoclave as that employed in Example A was charged with 200 g of PX, 5 g of PTA, and manganese acetate and nickel acetate each containing Mn and Ni of the amount specified in Table 6. (The total concentration of Mn and Ni of the catalyst was 546 ppm.) Air was blown into the system at such a rate as would make its flow rate at the exit 2.0 liters/min., at the temperature of 220°C. and pressure of 20 kg/cm²G, under high-speed agitation. After the oxygen absorption started, a liquid mixture of methanol and PX (mixing ratio=4:1 by volume) was fed into the system at the rate of 100 ml/min. Those conditions were maintained constant throughout the reaction (4 hours). The con-

densable gas failed to be caught at the condenser was passed through an exhaust gas-absorbing bottle, and trapped as dissolved in N,N-dimethylformamide.

After the reaction ended, the reaction mixture was cooled and withdrawn. The weight and composition of the reaction mixture and condensed liquid as well as the composition of the exhaust gas-absorbing liquid were measured, and from the results the yields of effective product based on PX and methanol were calculated according to the equations (I) and (II), respectively. Also the DMT formed (mmol) in the reaction mixture was divided by the reaction time to determine the formation rate of DMT.

The results were as shown in Table 6.

TABLE 6

Run No.	Catalyst		Mn : Ni (weight ratio)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/gr.)
	Mn (mgr)	Ni (mgr)				
F-1 (Control)	0	112	0:100	59.2	37.6	30.9
F-2 (Example)	28	84	25: 75	82.0	64.2	64.1
F-3 (do.)	56	56	50: 50	92.4	73.3	67.2
F-4 (do.)	84	28	75: 25	85.1	58.3	59.3
F-5 (Control)	112	0	100: 0	73.8	38.6	53.2
F-6*(do.)	0	0	—	69.0	43.4	38.9

*In Run No. F-6, cobalt acetate alone was used as the catalyst, the amount of which was 112 mgr. as converted to cobalt metal.

Example G.

The same autoclave as employed in Example A was used in the experiments of the operations similar to Example A. The initial feed was composed of 200 g of PX, 5 g of PTA, and acetate or acetates of manganese, nickel, or cobalt, containing respectively Mn, Ni, or Co of the amounts specified in Table 7. The total concentration of the catalytic components

calculated as the metals was invariably 546 ppm. The reaction temperature was 200°C., the pressure was 15 kg/cm²G, flow rate of air at the exit was 1.8 liters/min., feed rate of mixed liquid of methanol and PX (mixing ratio=4:1 by volume) was 80 ml/hr., and the reaction time was 4 hours.

The results were as shown in Table 7.

TABLE 7

Run No.	Catalyst Composition			Mn : Ni (weight ratio)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
	Mn (mgr)	Ni (mgr)	Co (mgr)				
G-1 (Control)	0	112	0	0:100	69.4	39.5	22.2
G-2 (Example)	28	84	0	25: 75	87.2	67.5	42.2
G-3 (do.)	56	56	0	50: 50	92.1	73.7	50.3
G-4 (do.)	84	28	0	75: 25	83.2	63.6	47.0
G-5 (Control)	112	0	0	100: 0	75.0	40.3	41.7
G-6 (do.)	0	0	112	—	73.3	46.5	31.0

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Example H.

Experiments were performed by the operation procedures similar to those of Example A,

using the identical autoclave. The initial feed was composed of 200 g of PX, 5 g of PTA, and manganese acetate and nickel acetate con-

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- 5 taining respectively the Mn and Ni of the amounts specified in Table 8. The catalyst concentration was in all runs 488 ppm. The reaction temperature was 180°C., the pressure was 10 kg/cm²G, flow rate of air at the exit was 1.5 liters/min., feed rate of the liquid mixture of methanol and PX (mixing ratio= 4:1 by volume) was 50 ml/hr., and the re- action time was 4 hours. The results were as shown in Table 8 below. 10

TABLE 8

Run No.	Catalyst		Yield of Products Based on PX (%)	Yield of Products Based on Methanol (%)	DMT Formation (mmol/hr.)
	Mn (mgr)	Ni (mgr)			
H-1 (Example)	50	50	88.6	67.7	28.3

Example I.

- 15 Experiments were performed by the operation procedures similar to those of Example A, using the identical autoclave. The initial feed was composed of 200 g of PX, 5 g of PTA, manganese acetate and nickel acetate of the amounts as would make the total concentration thereof as the metals 550 ppm. The ratio of Mn to Ni in the catalyst in each run was as specified in Table 9. The reaction temperature was 200°C., pressure was 15 kg/cm²G, flow rate of air at the exit was 2.0 liters/min., feed rate of the liquid mixture of methanol and PX (mixing ratio = 4:1 by volume) was 100 ml/hr., and the reaction time was 4 hours. The results were as shown also in Table 9. 25
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TABLE 9

Run No.	Mn:Ni (weight ratio)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
I-1 (Control)	0:100	68.5	38.9	21.8
I-2 (do.)	0.3:99.7	70.1	40.6	22.5
I-3 (do.)	0.7:99.3	71.4	41.7	22.8
I-4 (Example)	5:95	76.2	49.0	26.2
I-5 (do.)	10:90	80.8	55.5	30.9
I-6 (do.)	25:75	87.2	67.5	42.2
I-7 (do.)	50:50	91.9	74.2	50.0
I-8 (do.)	75:25	83.2	63.6	47.0
I-9 (Control)	98:2	75.4	42.3	42.0
I-10 (do.)	99.5:0.5	75.3	40.6	41.9
I-11 (do.)	100:0	75.1	39.7	41.8

In the Table above, the data of Run Nos. I—6 and I—8 are those of G—2 and G—4; respectively.

Example J.

- 5 Experiments were run by the similar operation procedures to those of Example A, using the identical autoclave. The initial feed was composed of 200 g of PX, 5 g of PTA, and manganese acetate and nickel acetate of the amounts as would make the weight ratio of

Mn to Ni as the metals 1:1. The total concentration of Mn plus Ni was varied for each run as specified in Table 10. The reaction temperature was 200°C., pressure was 15 kg/cm²G, flow rate of air at the exit was 2.0 litres/min., feed rate of the liquid mixture of methanol and PX (mixing ratio=4:1 by volume) was 100 ml/hr., and the reaction time was 4 hours.

The results were as shown in Table 10.

TABLE 10

Run No.	Catalyst Concentration (Mn + Ni, ppm)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
J-1 (Control)	10	The reaction failed to progress satisfactorily		
J-2 (Example)	100	71.8	56.3	30.1
J-3 (do.)	550	91.1	73.9	49.5
J-4 (do.)	1500	93.9	63.3	33.6
J-5 (do.)	5000	76.0	46.8	18.0

Example K.

- 25 Experiments were run in the manner similar to Example A, using the identical autoclave, at the reaction conditions specified for each run in Table 11. The initial feed was composed of 200 g of PX and 5 g of PTA.

As the catalyst, manganese acetate and nickel acetate were used at the weight ratio of 1:1 as converted respectively to Mn and Ni, the total concentration of Mn plus Ni being 550 ppm. The reaction time was 4 hours.

The results were as shown in Table 11.

TABLE 11

Run No.	Temp. (°C.)	Pressure (kg/cm ² G)	Feed Rate of Methanol + PX (ml/hr.)	Flow Rate of Air at Exit (l/min.)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
K-1 (Control)	120	3.0	50	1.5	The reaction failed to progress satisfactorily		
K-2 (do.)	140	3.5	50	1.5	93.5	25.0	0.3
K-3 (Example)	160	6.0	50	1.5	92.2	46.9	1.5
K-4 (do.)	180	10	50	1.5	90.8	66.4	28.3
K-5 (do.)	200	15	100	2.0	90.9	74.0	48.6
K-6 (do.)	220	20	100	2.0	90.1	72.9	66.0
K-7 (do.)	250	30	100	2.0	83.3	68.1	79.0
K-8 (do.)	275	35	100	2.0	75.3	60.8	80.8

Example L.

Experiments were run similarly to Example A, using the identical autoclave. The initial feed was composed of 200 g of PX and 5 g of PTA. As the catalyst manganese acetate, cobalt acetate, and nickel acetate were charged in the amounts as would make the weight ratio of Mn, Co, and Ni as the metals the values specified in Table 12, the total concentration

of the catalytic components as the metals being in all runs 550 ppm. The reaction temperature was 200°C., the pressure was 15 kg/cm²G, flow rate of air at the exit was 1.8 liters/min., feed rate of the liquid mixture of methanol and PX (mixing ratio=4:1 by volume) was 100 ml/hr., and the reaction time was 4 hours.

The results were as shown in Table 12.

TABLE 12

Run No.	Mn:Co:Ni (weight ratio)	Yield of Effective Products Based on PX (%)	Yield of Effective Products Based on Methanol (%)	DMT Formation Rate (mmol/hr.)
L-1 (Example)	40 : 40 : 20	88.7	51.4	44.2
L-2 (do.)	33.3:33.3:33.3	90.0	50.2	44.5
L-3 (do.)	40 : 20 : 40	90.8	50.2	43.1
L-4 (Control)	0 : 100 : 0	73.5	44.9	30.3
L-5 (do.)	100 : 0 : 0	75.7	39.7	40.8
L-6 (do.)	0 : 0 : 100	70.1	39.1	21.2

WHAT WE CLAIM IS:—

1. A process for the direct preparation of dimethyl terephthalate which comprises contacting molecular oxygen with a liquid phase reaction mixture comprising a catalyst, methanol and at least one aromatic compound selected from *p*-xylene and partial oxidation derivatives thereof, thus oxidising the methyl groups and/or partial oxidation derivatives thereof of the aromatic compound to carboxylic acid groups which are esterified *in situ* by the methanol to produce dimethyl terephthalate, wherein the reaction is performed.

(1) in the substantial absence of halogen and halogen-containing compounds;

(2) while maintaining the concentration of methanol in the reaction mixture at 0.5 to 15% by weight;

(3) in the presence of a catalyst composed of

(A) manganese metal or a manganese compound soluble in the reaction mixture and

(B) at least one metal compound selected from cobalt, nickel, cobalt compounds which are soluble in the reaction mixture and nickel compounds which are soluble in the reaction mixture, the weight ratio of (A) to (B) each calculated as the metal, being from 97:3 to 1:99 and the total concentration of (A) and (B), calculated as the metals, in the liquid phase reaction mixture being 100 to 10000 ppm when (B) is cobalt or a cobalt compound and 100 to 5000 ppm when (B) is nickel or a nickel compound;

(4) at a temperature of 160 to 280°C.

2. A process according to claim 1 wherein a mixture of said aromatic compounds is employed as starting material.

3. A process according to claim 2 wherein the desired product is separated from the reaction mixture and the residue is recycled.

4. A process according to claim 1, 2 or 3 wherein the catalyst comprises a manganese compound specifically named herein and a cobalt compound and/or nickel compound specifically named herein.

5. A process according to claim 4 wherein

the catalyst comprises manganese acetate, benzoate, toluate or naphthenate and cobalt and/or nickel acetate, benzoate, toluate or naphthenate.

6. A process according to any one of the preceding claims wherein (B) is cobalt or a cobalt compound, and the weight ratio of (A) to (B), each calculated as the metal, is 95:5 to 2:98.

7. A process according to claim 6 wherein the total concentration of (A) and (B) is 200 to 8,000 ppm.

8. A process according to claim 6 or 7 wherein the reaction temperature is 160 to 240°C.

9. A process according to claim 8, wherein the reaction temperature is 170 to 230°C.

10. A process according to any one of claims 1 to 5 wherein (B) is nickel or a nickel compound, and the weight ratio of (A) to (B), each calculated as the metal is 95:5 to 5:95.

11. A process according to claim 10 wherein the total concentration of (A) and (B), each calculated as the metal, is 200 to 4,000 ppm.

12. A process according to claim 10 or 11 wherein the reaction temperature is 170 to 270°C.

13. A process according to claim 12 wherein the reaction temperature is 180 to 250°C.

14. A process according to any one of the preceding claims wherein the concentration of methanol is maintained at 0.5 to 10% by weight.

15. A process according to claim 14 wherein the concentration is maintained at 0.5 to 8% by weight.

16. A process according to any one of the preceding claims wherein the reaction is carried out under a pressure of 1 to 200 kg/cm².

17. A process according to claim 1 substantially as described in any one of the foregoing Examples.

18. Dimethyl terephthalate when prepared by a process as claimed in any one of the preceding claims.

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